Multifunctional fluorescence responses of phenyl-amide-bridged d¹⁰ coordination polymers structurally regulated by dicarboxylates and metal ions

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Supporting Information

Materials and Methods

The ligand L was synthesized according to the previous literature.[S1] All reagents and solvents were purchased directly from commercial sources without further purification. Powder X-ray diffraction (PXRD) data was measured on a D/teX superdiffractometer (Cu-K α , $\lambda = 1.5406$). IR absorption spectrum (KBr precipitation) in the range 4000–500 cm⁻¹ was recorded on a Varian 640 FT-IR spectrometer. The fluorescence spectrum was tested at 296 K on a Hitachi F-4500 fluorescence spectrometer. UV-vis absorption spectra were carried out on Perkin Elmer Lambda 750. The fluorescence lifetime could be obtained with a FLS1000 Transient Steady-state Fluorescence Spectrometer.

X-ray Crystallography

X-ray single-crystal diffraction data for 1–4 were collected on a Bruker SMART APEX II diffractometer with MoK α radiation ($\lambda = 0.71073$ Å). The related crystal structure is solved by using the SHELXS program of the SHELXTL crystallography software package by the direct method and further improving on F^2 by the full matrix least square method.[S2] The non-hydrogen atoms were refined by anisotropic temperature parameters, the hydrogen atoms of the organic ligands were placed at calculated positions and treated with riding atoms whose isotropic displacement parameters were set at 1.2–1.5 times the U_{eq} values of the parent atoms. Table 1 is the details of the crystal data and structure refinement of 1–4. Tables S1–S4 (supporting information) are the selected bond length (Å) and angle (deg) CCDC numbers for 1–4 were 1975907, 1975908, 1975909 and 1975911, respectively. Crystallographic data can be collected free of charge at <u>www.ccdc.cam.ac.uk/conts/retrieving.html</u>.

	1		
Zn(1)-O(5)A	1.9202(13)	O(5)A-Zn(1)-N(4)	107.32(7)
Zn(1)-O(4)	1.9367(15)	O(4)–Zn(1)–N(4)	114.31(7)
Zn(1)–N(4)	2.0405(16)	O(5)A-Zn(1)-N(1)B	95.82(6)
Zn(1)–N(1)B	2.0759(16)	O(4)–Zn(1)–N(1)B	95.75(7)
O(5)A–Zn(1)–O(4)	130.40(7)	N(4)-Zn(1)-N(1)B	108.16(6)

Table S1. Selected bond distances (Å) and angles (°) for 1.

Symmetry code: A: -x + 3/2, y + 1/2, -z + 3/2; B: -x + 1, -y + 1, -z + 1

	2		
Zn(1)-O(3)A	1.9178(18)	O(3)A–Zn(1)–N(2)	120.89(9)
Zn(1)–O(1)	1.9394(17)	O(1)–Zn(1)–N(2)	97.62(8)
Zn(1)–N(2)	2.036(2)	O(3)A–Zn(1)–N(1)	110.99(9)
Zn(1)–N(1)	2.076(2)	O(1)–Zn(1)–N(1)	102.69(9)
O(3)A–Zn(1)–O(1)	122.57(9)	N(2)–Zn(1)–N(1)	98.11(9)

Table S2. Selected bond distances (Å) and angles (°) for 2.

Symmetry code: A: x - 1, y, z

Table S3. Selected bond distances (Å) and angles (°) for 3.

3					
Zn(1)–O(4)	2.0336(16)	O(4)–Zn(1)–N(1)	93.85(6)		
Zn(1)–N(3)	2.0853(16)	N(3)–Zn(1)–N(1)	103.64(7)		
Zn(1)–O(5)A	2.0891(19)	O(5)A–Zn(1)–N(1)	103.03(7)		
Zn(1)–N(1)	2.0933(16)	O(4)–Zn(1)–O(6)A	100.84(6)		
O(4)–Zn(1)–N(3)	104.37(6)	N(3)–Zn(1)–O(6)A	148.43(7)		
O(4)–Zn(1)–O(5)A	153.55(7)	O(5)A–Zn(1)–O(6)A	58.50(6)		
N(3)–Zn(1)–O(5)A	91.40(7)	N(1)–Zn(1)–O(6)A	93.21(7)		

Symmetry code:A: -x + 3/2, y + 1/2, -z + 3/2

Table S4. Selected bond distances (Å) and angles (°) for 4.

4					
Cd(1)-O(2)A	2.2328(14)	O(1W)–Cd(1)–O(4)	86.05(5)		
Cd(1)–N(1)	2.2545(14)	O(2)A-Cd(1)-O(3)	99.76(5)		
Cd(1)-O(1W)	2.2809(14)	N(1)-Cd(1)-O(3)	92.27(5)		
Cd(1)–O(4)	2.3019(13)	O(1W)-Cd(1)-O(3)	136.76(5)		
Cd(1)–O(3)	2.4303(12)	O(4)-Cd(1)-O(3)	55.08(4)		
Cd(1)-O(1)A	2.5026(14)	O(2)A-Cd(1)-O(1)A	54.44(5)		
O(2)A-Cd(1)-N(1)	143.38(6)	N(1)-Cd(1)-O(1)A	92.07(5)		
O(2)A-Cd(1)-O(1W)	103.53(6)	O(1W)-Cd(1)-O(1)A	91.42(5)		
N(1)-Cd(1)-O(1W)	90.23(5)	O(4)-Cd(1)-O(1)A	149.95(5)		
O(2)A-Cd(1)-O(4)	97.08(5)	O(3)-Cd(1)-O(1)A	131.56(5)		
N(1)-Cd(1)-O(4)	117.86(5)				

Symmetry code: A: -x - 1, -y + 1, -z + 1



Fig. S1 The IR spectra of 1–4.

The infrared spectra of **1–4** were measured in the frequency range of 4000–500cm⁻¹. As shown in Fig S1, the amino stretching vibration of the ligand in **1–4** were at 756, 731, 712 and 699cm⁻¹, respectively.[S3] The methylene stretching vibration peaks of **1–4** were 2909, 2921, 2946 and 2934cm⁻¹. The peaks of methylene of ligand **1–4** were at 2909, 2921, 2946 and 2934cm⁻¹.[S4] The stretching vibration peaks of –OH in water molecules were 3335, 3309, 3247 and 3222cm⁻¹.[S5]



Fig. S2 (a) $[Zn-(1,3-BDC)]_n$ chain of 2. (b) $[Zn-L]_n$ chain of 2. (c) Schematic view of 2D network.



Fig. S3 (a) [Zn-(1,2-BDC)]_{*n*} chain of **3**. (b) [Zn-L]_{*n*} chain of **3**.



Fig. S4 Schematic view of 1D structure of 4.



Fig. S5 The changes of PXRD patterns of five complexes in different pH solutions.

In order to prove the phase purity of the five complexes, powder X-ray diffraction testing was performed. As shown in Fig. S5, the experimental peaks and simulated peaks of **1–4** and **1a** basically coincide. The result was proved that the purity of the sample was good.



Chart S1 The structural details of 1–4 and 1a. (a and h) The schematic view of the structures; (b and g) L ligands; (c and f) The coordination modes of metal ions. (d and e) Dicarboxylates.



Fig. S6 Histogram of the fluorescence emission intensity of 1–4, 1a in different cation solutions.



Fig. S7 (a) Fluorescence emission intensity of **2** in different cation solutions. (b) Fe^{3+} concentration gradient. (c) SV plot of **2** for sensing of Fe^{3+} ions. (d) Fluorescence emission intensities of **2** at room temperature upon the addition of Fe^{3+} or Fe^{3+} + interference ions.



Fig. S8 (a) Fluorescence emission intensity of **3** in different cation solutions. (b) Fe^{3+} concentration gradient. (c) SV plot of **3** for sensing of Fe^{3+} ions. (d) Fluorescence emission intensities of **3** at room temperature upon the addition of Fe^{3+} or Fe^{3+} + interference ions.



Fig. S9 (a) Fluorescence emission intensity of **4** in different cation solutions. (b) Fe^{3+} concentration gradient. (c) SV plot of **4** for sensing of Fe^{3+} ions. (d) Fluorescence emission intensities of **4** at room temperature upon the addition of Fe^{3+} or Fe^{3+} + interference ions.



Fig. S10 (a) Fluorescence emission intensity of **1a** in different cation solutions. (b) Fe^{3+} concentration gradient. (c) SV plot of **1a** for sensing of Fe^{3+} ions. (d) Fluorescence emission intensities of **1a** at room temperature upon the addition of Fe^{3+} or Fe^{3+} + interference ions.



Fig. S11 (a) Fluorescence emission intensity of 2 in different anions solutions. (b) Histogram of fluorescence emission intensity in different anion solutions. (c) and (d) CrO₄²⁻, Cr₂O₇²⁻ concentration gradient. (e) and (f) SV plot of 2 for sensing of CrO₄²⁻, Cr₂O₇²⁻ anions. (g) and (h) Fluorescence intensity of CrO₄²⁻, Cr₂O₇²⁻ before and after adding interference anions.



Fig. S12 (a) Fluorescence emission intensity of 3 in different anions solutions. (b) Histogram of fluorescence emission intensity in different anion solutions. (c) and (d) CrO₄²⁻, Cr₂O₇²⁻ concentration gradient. (e) and (f) SV plot of 3 for sensing of CrO₄²⁻, Cr₂O₇²⁻ anions. (g) and (h) Fluorescence intensity of CrO₄²⁻, Cr₂O₇²⁻ before and after adding interference anions.



Fig. S13 (a) Fluorescence emission intensity of 4 in different anions solutions. (b) Histogram of fluorescence emission intensity in different anion solutions. (c) and (d) CrO₄²⁻, Cr₂O₇²⁻ concentration gradient. (e) and (f) SV plot of 4 for sensing of CrO₄²⁻, Cr₂O₇²⁻ anions. (g) and (h) Fluorescence intensity of CrO₄²⁻, Cr₂O₇²⁻ before and after adding interference anions.



Fig. S14 (a) Fluorescence emission intensity of 1a in different anions solutions. (b) Histogram of fluorescence emission intensity in different anion solutions. (c) and (d) CrO₄²⁻, Cr₂O₇²⁻ concentration gradient. (e) and (f) SV plot of 1a for sensing of CrO₄²⁻, Cr₂O₇²⁻ anions. (g) and (h) Fluorescence intensity of CrO₄²⁻, Cr₂O₇²⁻ before and after adding interference anions.



Fig. S15 Histogram of the fluorescence emission intensity of 1–4, 1a in different pesticide solutions.



Fig. S16 (a) Fluorescence emission intensity of 2 in different pesticide solutions. (b) 2,6-DC-4-NA concentration gradient. (c) SV plot of 2 for sensing of 2,6-DC-4-NA. (d) Fluorescence emission intensities of 2 at room temperature upon the addition of 2,6-DC-4-NA or 2,6-DC-4-NA +

interference pesticides.



Fig. S17 (a) Fluorescence emission intensity of 3 in different pesticide solutions. (b) 2,6-DC-4-NA concentration gradient. (c) SV plot of 3 for sensing of 2,6-DC-4-NA. (d) Fluorescence emission intensities of 3 at room temperature upon the addition of 2,6-DC-4-NA or 2,6-DC-4-NA + interference pesticides.



Fig. S18 (a) Fluorescence emission intensity of 4 in different pesticide solutions. (b) 2,6-DC-4-NA concentration gradient. (c) SV plot of 4 for sensing of 2,6-DC-4-NA. (d) Fluorescence emission intensities of 4 at room temperature upon the addition of 2,6-DC-4-NA or 2,6-DC-4-NA + interference pesticides.



Fig. S19 (a) Fluorescence emission intensity of **1a** in different pesticide solutions. (b) 2,6-DC-4-NA concentration gradient. (c) SV plot of **1a** for sensing of 2,6-DC-4-NA. (d) Fluorescence emission intensities of **1a** at room temperature upon the addition of 2,6-DC-4-NA or 2,6-DC-4-NA + interference pesticides.



Fig. S20 (a)–(e) Cyclic experiments of 1–4, 1a, blue is the original intensity, red is the fluorescence intensity after adding 2,6-DC-4-NA.



Fig. S21 PXRD patterns of 1.



Fig. S22 UV-Vis absorption spectra of Fe³⁺, CrO₄²⁻, Cr₂O₇²⁻ and 2,6-DC-4-NA solutions and the



emission spectrum of 1.

Fig. S23 Lifetime decay curves of 1 before and after the addition of four analyses.

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